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WO 01/12542 A1

(54) Title: PROCESS FOR PRODUCING Mg-CONTAINING NON-AI ANIONIC CLAY

(57) Abstract: This patent describes economical and environment-friendly processes for the synthesis of Mg-containing non-AI anionic clays. It involves (hydro)thermally reacting a slurry comprising a Mg metals source with a trivalent metals source to directly obtain Mg-containing non-AI anionic clay, the Mg sources being an oxide, hydroxide or a carbonate. There is no necessity to wash or filter the product. It can be spray dried directly to form microspheres or can be extruded to form shaped bodies. The product can be combined with other ingredients in the manufacture of catalysts, absorbents, pharmaceuticals, cosmetics, detergents, and other commodity products that contain anionic clays.

## PROCESS FOR PRODUCING Mg-CONTAINING NON-AI ANIONIC CLAY

## 5 BACKGROUND OF THE INVENTION

This invention involves the preparation of Mg-containing non-AI anionic clays. Anionic clays have a crystal structure which consists of positively charged layers built up of specific combinations of metal hydroxides  
10 between which there are anions and water molecules. Hydrotalcite is an example of a naturally occurring anionic clay, in which carbonate is the predominant anion present. Meixnerite is an anionic clay wherein  $\text{OH}^-$  is the predominant anion present.

15 In hydrotalcite-like anionic clays the brucite-like main layers are built up of octahedra alternating with interlayers in which water molecules and anions, more particularly carbonate ions, are distributed. The interlayers contain anions such as  $\text{NO}_3^-$ ,  $\text{OH}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{SiO}_3^{2-}$ ,  $\text{CrO}_4^{2-}$ ,  $\text{BO}_3^{2-}$ ,  $\text{MnO}_4^-$ ,  $\text{HGaO}_3^{2-}$ ,  $\text{HVO}_4^{2-}$ ,  $\text{ClO}_4^-$ ,  $\text{BO}_3^{2-}$ , pillaring anions such as  $\text{V}_{10}\text{O}_{28}^{6-}$  and  
20  $\text{MO}_7\text{O}_{24}^{6-}$ , monocarboxylates such as acetate, dicarboxylates such as oxalate, alkyl sulphonates such as laurylsulphonate.

It should be noted that a variety of terms is used to describe the material which is referred to in this patent as an anionic clay. Hydrotalcite-like and  
25 layered double hydroxide are interchangeably used by those skilled in the art. In this patent application we refer to the materials as anionic clays, comprising within that term hydrotalcite-like and layered double hydroxide materials.

The most commonly described anionic clays are Mg-Al anionic clays. In the prior art the emphasis is usually on this type of anionic clays, whereas the Mg-containing non-Al anionic clays are only mentioned in passing, even though the chemistry of their preparation and their properties can be very different and unpredictable. Mg-Al anionic clays are suitable for many applications in the absorbent and catalysts field, but Mg-containing non-Al anionic clays have specific applications in these fields.

The preparation of anionic clays has been described in many prior art publications.

Two major reviews of anionic clay chemistry were published in which the synthesis methods available for anionic clay synthesis have been summarized, F. Cavani et al "Hydrotalcite-type anionic clays: Preparation, Properties and Applications," Catalysis Today, 11 (1991) Elsevier Science Publishers B. V. Amsterdam.

J P Besse and others "Anionic clays: trends in pillaring chemistry, its synthesis and microporous solids"(1992), 2, 108, editors: M.I. Occelli, H.E. Robson, Van Nostrand Reinhold, N.Y.

In these reviews basically two types of anionic clay preparation are described. The most conventional method is co-precipitation (in Besse this method is called the salt-base method) of a soluble divalent metal salt and a soluble trivalent metal salt, optionally followed by hydrothermal treatment or aging to increase the crystallite size. The second method is the salt-oxide method in which a divalent metal oxide is reacted at atmospheric pressure with a soluble trivalent metal salt, followed by aging under atmospheric pressure. This method has only been described for the use of ZnO and CuO in combination with soluble trivalent metal salts.

For work on anionic clays, reference is given to the following articles:

Helv. Chim. Acta, 25, 106-137 and 555-569 (1942)

J. Am. Ceram. Soc., 42, no. 3, 121 (1959)

Chemistry Letters (Japan), 843 (1973)

5 Clays and Clay Minerals, 23, 369 (1975)

Clays and Clay Minerals, 28, 50 (1980)

Clays and Clay Minerals, 34, 507 (1996)

Materials Chemistry and Physics, 14, 569 (1986).

10 In addition there is an extensive amount of patent literature on the use of anionic clays and processes for their preparation.

European Patent Application 0 536 879 describes a method for introducing pH-dependent anions into the clay. The clay is prepared by the addition of a solution of  $\text{Al}(\text{NO}_3)_3$  and  $\text{Mg}(\text{NO}_3)_2$  to a basic solution containing borate  
15 anions. The product is then filtered, washed repeatedly with water, and dried overnight. Additionally mixtures of Zn/Mg are used.

In US 3,796,792 by Miyata et al. entitled "Composite Metal Hydroxides" a range of materials is prepared into which an extensive range of cations is  
20 incorporated, including Sc, La, Th, In, etc. In the examples given solutions of the divalent and trivalent cations are prepared and mixed with base to cause co-precipitation. The resulting products are filtered, washed with water, and dried at 80 °C. Example 1 refers to Mg and Sb and Example 3 to Mg and Bi. Other examples are given, and in each case soluble salts are  
25 used to make solutions prior to precipitation of the anionic clay at high pH.

In US 3,879,523 by Miyata entitled "Composite Metal Hydroxides" also a large number of preparation examples is outlined. The underlying chemistry, however, is again based on the co-precipitation of soluble salts

followed by washing and drying. It is important to emphasize that washing is a necessary part of such preparations, because to create a basic environment for co-precipitation of the metal ions a basic solution is needed and this is provided by NaOH/Na<sub>2</sub>CO<sub>3</sub> solutions. Residual sodium, for example, can have a significant deleterious effect on the subsequent performance of the product as a catalyst or oxide support.

In US 3879525 (Miyata) very similar procedures are again described.

10 In US 4,351,814 to Miyata et al. a method for making fibrous hydrotalcites is described. Such materials differ in structure from the normal plate-like morphology. The synthesis again involves soluble salts. For example, an aqueous solution of a mixture of MgCl<sub>2</sub> and CaCl<sub>2</sub> is prepared and suitably aged. From this a needle-like product Mg<sub>2</sub>(OH)<sub>3</sub>Cl.4H<sub>2</sub>O precipitates. A  
15 separate solution of sodium aluminate is then reacted in an autoclave with the solid Mg<sub>2</sub>(OH)<sub>3</sub>Cl.4H<sub>2</sub>O and the product is again filtered, washed with water, and dried.

In US 4,458,026 to Reichle, in which heat-treated anionic clays are  
20 described as catalysts for aldol condensation reactions, again use is made of magnesium and aluminium nitrate salt solutions. Such solutions being added to a second solution of NaOH and Na<sub>2</sub>CO<sub>3</sub>. After precipitation the slurry is filtered and washed twice with distilled water before drying at 125 °C.

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In US 4,656,156 to Misra the preparation of a novel absorbent based on mixing activated alumina and hydrotalcite is described. The hydrotalcite is

made by reacting activated MgO (prepared by activating a magnesium compound such as magnesium carbonate or magnesium hydroxide) with aqueous solutions containing aluminate, carbonate and hydroxyl ions. As an example the solution is made from NaOH, Na<sub>2</sub>CO<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub>. In particular, the synthesis involves the use of industrial Bayer liquor as the source of Al. The resulting products are washed and filtered before drying at 105 °C.

In US 4,904,457 to Misra a method is described for producing hydrotalcites in high yield by reacting activated magnesia with an aqueous solution containing aluminate, carbonate, and hydroxyl ions.

The methodology is repeated in US 4,656,156.

In US 5,507,980 to Kelkar et al. a process is described for making novel catalysts, catalyst supports, and absorbers comprising synthetic hydrotalcite-like binders. The synthesis of the typical sheet hydrotalcite involves reacting pseudo-boehmite to which acetic acid has been added to peptize the pseudo-boehmite. This is then mixed with magnesia. More importantly, the patent summary states clearly that the invention uses mono carboxylic organic acids such as formic, propionic and isobutyric acid. In this patent the conventional approaches to preparing hydrotalcites are presented.

In US 6,539,861 a process is disclosed for preparing a catalysts for synthesis gas production based on hydrotalcites. The method of preparation is again based, on the co-precipitation of soluble salts by mixing with base, for example, by the addition of a solution of RhCl<sub>3</sub>,

Mg(NO<sub>3</sub>)<sub>2</sub> and Al(NO<sub>3</sub>)<sub>3</sub> to a solution of Na<sub>2</sub>CO<sub>3</sub> and NaOH.

Also in US 5,399,537 to Bhattacharyya in the preparation of nickel-containing catalysts based on hydrotalcite use is made of the co-precipitation of soluble magnesium and aluminium salts.

In US 5,591,418 to Bhattacharyya a catalyst for removing sulfur oxides or nitrogen oxides from a gaseous mixture is made by calcining an anionic clay, said anionic clay having been prepared by co-precipitation of a solution of Mg(NO<sub>3</sub>)<sub>2</sub>, Al(NO<sub>3</sub>)<sub>3</sub> and Ce(NO<sub>3</sub>)<sub>3</sub>. The product again is filtered and repeatedly washed with de-ionized water.

In US 5,114,898/WO 9110505 Pinnavaia et al. describe layered double hydroxide sorbents for the removal of sulfur oxide(s) from flue gases, which layered double hydroxide is prepared by reacting a solution of Al and Mg nitrates or chlorides with a solution of NaOH and Na<sub>2</sub>CO<sub>3</sub>. In US 5,079,203 /WO 9118670 layered double hydroxides intercalated with polyoxo anions are described, with the parent clay being made by co-precipitation techniques.

20

In US 5,578,286 in the name of Alcoa a process for the preparation of meixnerite is described. Said meixnerite may be contacted with a dicarboxylate or polycarboxylate anion to form a hydrotalcite-like material.

25 In US 4,946,581 and US 4,952,382 to van Broekhoven co-precipitation of soluble salts such as Mg(NO<sub>3</sub>)<sub>2</sub> and Al(NO<sub>3</sub>)<sub>3</sub> with, and without the incorporation of rare earth salts was used for the preparation of anionic

clays as catalyst components and additives. A variety of anions and di- and tri-valent cations are described.

As indicated in the description of the prior art given-above, there are many applications of anionic clays.

These include but are not restricted to: catalysts, adsorbents, drilling muds, catalyst supports and carriers, extenders and applications in the medical field. In particular van Broekhoven has described their use in SO<sub>x</sub> abatement chemistry.

10

Because of this wide variety of large-scale commercial applications for these materials, new processes utilizing alternative inexpensive raw materials are needed to provide a more cost-effective and environmentally compatible processes for making anionic clays. In particular, from the prior art described above one can conclude that the preparation process can be improved in the following ways: the use of cheaper sources of reactants, processes for easier handling of the reactants, so that there is no need for washing or filtration, eliminating the filtration problems associated with these fine-particled materials, the avoidance of alkali metals (which can be particularly disadvantageous for certain catalytic applications): Further, in drying or calcining the anionic clay prepared by prior art processes gaseous emissions of nitrogen oxides, halogens, sulfur oxides, etc. are encountered which cause environmental pollution problems.

25

#### SUMMARY OF THE INVENTION

Our invention includes processes for producing Mg-containing non-Al anionic clays using relatively inexpensive starting materials in a simple



process which involves reacting mixtures with or without stirring in water, optionally under hydrothermal conditions. Such processes can be operated in standard laboratory/industrial equipment. More specifically, there is no need for washing or filtering, and a wide range of ratios of Mg(II)/M(III) in the reaction product is possible.

This invention involves the use of an aluminum source and a divalent metal source in aqueous suspensions, which are reacted, optionally under hydrothermal conditions and the reaction mixture results in the direct formation of a Mg-containing non-Al anionic clay. The powder X-ray diffraction pattern (PXRD) suggests that the product is comparable to anionic clays made by other standard methods. The physical and chemical properties of the product are also comparable to those anionic clays made by the other conventional methods. The overall process of this invention is very flexible, enabling a wide variety of anionic clay compositions and anionic clay-like materials involving for example carbonate, hydroxide and other anions to be prepared in an economically and environmental-friendly manner. The process may be carried out in a one-step process either in batch or in continuous mode.

## DETAILED DESCRIPTION OF THE INVENTION

This invention involves the preparation of Mg-containing non-Al anionic clays. In particular it describes a process for the preparation of an anionic clay wherein a suspension comprising a trivalent metal source and a Mg source is provided and reacted thermally or hydrothermally to obtain a Mg-containing non-Al anionic clay, the magnesium source being an oxide, a hydroxide, a hydroxycarbonate, or a carbonate.

It was found that Mg-containing non-Al anionic clays are directly obtained from the reaction according to the invention. This is in contrast to the

- coprecipitation method wherein soluble salts are first precipitated, filtered, washed to remove unwanted ions and then aged either hydrothermally or not. With the process according to the invention the presence of unwanted ions in the product can be avoided, as will be explained below. The
- 5 magnesium source is an oxide, hydroxide a hydroxy carbonate or carbonate. From this compound no ions beside hydroxide and carbonate end up in the anionic clay, which are the normal building blocks of anionic clays. If for the trivalent metal source a compound is chosen with harmless ions such as nitrate or acetate washing and filtration of the reaction product
- 10 can be avoided altogether. In fact, it was found that the reaction also takes place when using hydroxides, oxides, hydroxycarbonates or carbonates for both the divalent metal source and the trivalent metal source, in which case also no washing and filtration has to take place.
- 15 Since the process disclosed in this patent does not require washing of the product or filtering, there is no filtrate waste or gaseous emissions (e.g. from acid decomposition), making the process particularly environmental-friendly and more suited to the environmental constraints which are increasingly imposed on commercial operations. The product can be spray
- 20 dried directly to form microspheres or can be extruded, pelletized or beaded to form shaped bodies.

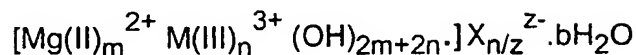
Anionic clays prepared by this method exhibit the well known properties and characteristics (e.g. chemical analysis, powder X-ray diffraction

25 pattern, FTIR, thermal decomposition characteristics, surface area, pore volume, and pore size distribution) usually associated with anionic clays prepared by the customary and previously disclosed methods.

The anionic clay according to the invention has a layered structure

10

corresponding to the general formula



- 5    Wherein m and n have a value such that m/n=1 to 10, preferably 1 to 6, and b has a value in the range of from 0 to 10, generally a value of 2 to 6 and often a value of about 4. X may be  $\text{CO}_3^{2-}$ ,  $\text{OH}^-$  or any other anion normally present in the interlayers of anionic clays. It is more preferred that m/n should have a value of 2 to 4, more particularly a value close to 3.

10

#### The trivalent metal source

- Suitable trivalent metal sources are compounds containing  $\text{Al}^{3+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Co}^{3+}$ ,  $\text{Ni}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{B}^{3+}$ , trivalent rare earth metal cations such
- 15    as  $\text{La}^{3+}$  and  $\text{Ce}^{3+}$ ,  $\text{Ga}^{3+}$  or mixtures of said compounds. Preferably oxides, hydroxides and carbonates of these metals are used, but also nitrate chlorides, sulfates and phosphates can be used. In the case of aluminium, the following compounds are suitable trivalent metals sources for the process of the invention: aluminium trihydrate (e.g. Gibbsite, BOC or
- 20    bayerite), and its thermally treated forms, flash calcined gibbsite, boehmite, aluminium salts such as aluminium nitrate, aluminium chloride, aluminium chlorohydrate, amorphous gel aluminas and sodium aluminate.

#### Divalent metal source

25

Suitable Mg sources are  $\text{MgO}$ ,  $\text{Mg}(\text{OH})_2$ , magnesium carbonate, and

magnesium bicarbonate. In addition to the Mg source other divalent metal source may be added such as compounds containing  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cu}^{2+}$ , and mixtures of said compounds. Preferably oxides, hydroxides and carbonates of these metals  
5 are used, but also nitrates chlorides, sulfates and phosphates can be used.

### Conditions

As mentioned above, the reaction is conducted under thermal or  
10 hydrothermal conditions. Within the context of this description hydrothermal means in the presence of water at a temperature above 100 °C at increased pressure. Thermal means at a temperature between ambient and 100 °C. Preferably the reaction takes place in water in an autoclave at a temperature above 100 °C, i.e. under autogeneous pressure.  
15 It is possible to purge the suspension with nitrogen or inert gas if an anionic clay with predominantly hydroxide anions are desired, but in general this is not necessary. Thus, the reaction can be conducted in the presence of  $\text{CO}_2$ . Said  $\text{CO}_2$  may be the  $\text{CO}_2$  normally present in air or it may be added to the reaction, for instance, by using a carbonate divalent or trivalent metal  
20 source.

Said aqueous suspension may be obtained by either combining slurries of the starting materials or adding *divalent metal source* to a slurry of *trivalent metal source* or vice versa. There is no need to wash or filter the product,  
25 as unwanted ions (e.g. sodium, ammonium, chloride, sulfate) which are frequently encountered when using other preparation methods, are absent in the product. If desired a preformed anionic clay may be added to the reaction mixture. Said preformed clay may be recycled anionic clay from

the reaction mixture or anionic clay made separately by the process according to the invention or any other process.

Because of its simplicity, this process can be carried out in a continuous mode by mixing of a first slurry comprising boehmite and a second slurry comprising magnesium source passing the mixed slurry through a reactor vessel which can operate under hydrothermal conditions. Said first and/or second slurry may be subjected to a treatment prior to mixing the slurries. Said pre-treatment may involve treatment with acid, base treatment, thermal and/or hydrothermal treatment, all optionally in the presence of seeds or combinations thereof.

As mentioned-above, if desired inorganic acids and bases, for example for control of the pH, may be added to the slurry before or during reaction or to the individual reactants before combining them in the slurry. The acid and bases of choice are formic acid, acetic acid, nitric acid and ammonium hydroxide, because these types of acids and bases do not introduce unwanted ions in the reaction mixture.

The most preferred combination of a divalent metal source and a trivalent metal sources is Ga-Mg, because these combinations result in Mg-containing non-Al anionic clays with specific applications in the catalyst field.

If desired, the anionic clay prepared by the process according to the invention may be subjected to ion exchange. Upon ion exchange the interlayer charge-balancing anions are replaced with other anions. Said other anions are the ones commonly present in anionic clays and include pillaring anions such as  $V_{10}O_{28}^{6-}$ ,  $Mo_7O_{24}^{6-}$ . Said ion exchange can be

conducted before drying or after the anionic clay formed in the slurry.

The process of the invention provides wide flexibility in preparing products with a wide range of M(II):M(III) ratios. The M(II):M(III) ratio can vary from  
5 0.1 to 10 , preferably from 1 to 6, more preferred from 2 to 4, and especially preferred to close to 3.

For some applications it is desirable to have additives, both metals and non-metals, such as rare earth metals, Si, P, B, group VI, group VIII,  
10 alkaline earth (for instance Ca and Ba) and/or transition metals (for example Mn, Fe, Ti, Zr, Cu, Ni, Zn, Mo, Sn), present. Said metals can easily be deposited on the anionic clay. They can also be added either to the divalent metal source or the trivalent metal source or to the slurry during preparation of the anionic clay.

15

The present invention is illustrated by the following examples which are not to be considered limitative by any means.

## EXAMPLES

Example 1

5

A slurry was provided of gallium nitrate and MgO with a Mg/Ga ratio of 2.3.

The pH of the slurry was adjusted to 10.02 with  $\text{NH}_3\text{OH}$ . The slurry was

subjected to hydrothermal treatment in an autoclave at 120 °C for 1 hour.

The product was dried at 110 °C. X-ray diffraction confirmed the formation

10 of a Mg-Ga anionic clay.

Example 2

A slurry was provided of gallium oxide and MgO with a Mg/Ga ratio of 2.3.

15 The pH of the slurry was adjusted to 10.2 with  $\text{NH}_3\text{OH}$ . The slurry was

subjected to thermal treatment at 90 °C for 18 hours. The product was

dried at 110 °C. X-ray diffraction confirmed the formation of a Mg-Ga

anionic clay.

20 Example 3

A slurry was provided of gallium oxide and MgO with a Mg/Ga ratio of 2.3.

The pH of the slurry was adjusted to 10.2 with  $\text{NH}_3\text{OH}$ . The slurry was

subjected to thermal treatment at 120 °C for 18 hours. The product was

25 dried at 110 °C. X-ray diffraction confirmed the formation of a Mg-Ga

anionic clay.

Example 4

A slurry was provided of gallium oxide and MgO with a Mg/Ga ratio of 2.3. The pH of the slurry was adjusted to 10.2 with  $\text{NH}_3\text{OH}$ . The slurry was subjected to hydrothermal treatment at 198 °C for 1 hour. The product was dried at 110 °C. X-ray diffraction confirmed the formation of a Mg-Ga anionic clay.



## Claims:

1. A process for the preparation of a Magnesium-containing non-Al anionic clay wherein a suspension comprising a trivalent metal source and a divalent metal source is provided and reacted to obtain a magnesium- containing non-Al anionic clay, the Magnesium source being an oxide, a hydroxide, a hydroxycarbonate or a carbonate.
2. A process according to claim 1 wherein the trivalent metal source is a compound containing  $\text{Al}^{3+}$ ,  $\text{Mn}^{3+}$ ,  $\text{Co}^{3+}$ ,  $\text{Ni}^{3+}$ ,  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ga}^{3+}$ ,  $\text{Sc}^{3+}$ ,  $\text{B}^{3+}$ , trivalent rare earth cations such as  $\text{La}^{3+}$  and  $\text{Ce}^{3+}$  or a mixture of said compounds.
3. A process according to any one of claims 1-2 wherein in addition to the magnesium source an additional the divalent metal source is added which is a compound containing  $\text{Ca}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Cu}^{2+}$ , and mixtures of said compounds.
4. A process according to any one of claims 1-3 wherein both the divalent metal source and the trivalent metal source are oxides, hydroxides or carbonates.
5. A process according to any one of claims 1-4 wherein acid or base is present in the slurry.
6. A process according to any one of preceding claims 1-5 wherein the process is carried out in a continuous mode.

7. A process according to any one of claims 1-6 wherein additives are present in the slurry.
- 5 8. A process according to any one of claims 1-7 wherein the Mg-containing non-Al anionic clay is subjected to an ion-exchange treatment.
9. A process according to claim 8 wherein the Mg-containing non-Al  
10 anionic clay is ion exchanged with pillaring anions such as  $V_{10}O_{28}^{6-}$   
and  $Mo_7O_{24}^{6-}$ .
10. Process according to any one of claims 1-9 wherein additives are deposited on the Mg-containing non-Al anionic clay.

15

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/07782

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01B13/36 C01G15/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01B C01G C01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, CHEM ABS Data

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 879 523 A (MIYATA SHIGEO ET AL) 22 April 1975 (1975-04-22) cited in the application column 15, line 36 - line 40; claims	1-7, 10
Y	---	8, 9
X	US 5 518 704 A (KELKAR CHANDRASHEKHAR P ET AL) 21 May 1996 (1996-05-21) cited in the application claim 17	1-7, 10
Y	---	8, 9
Y	US 5 079 203 A (KWON TAEHYUN ET AL) 7 January 1992 (1992-01-07) the whole document	8, 9
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

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Date of the actual completion of the international search

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# INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 00/07782

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 98 51615 A (ARISTECH CHEMICAL CORP) 19 November 1998 (1998-11-19) claim 1 ---	1
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Information on patent family members

International Application No

PCT/EP 00/07782

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